Barium cycling in the North Pacific: Implications for the utility of Ba as a paleoproductivity and paleoalkalinity proxy

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Abstract. Benthic incubation chambers have been deployed in a variety of geochemical environments that provide a comprehensive geochemical framework from which to address issues related to Ba geochemistry and the use of Ba as a paleoproxy. First order budgets for barium show that in the equatorial Pacific, present rates of Ba rain and benthic remobilization are nearly in balance, indicating that the rate of net accumulation is negligible and is clearly much less than the average for the Holocene; thus any paleoproxy algorithms built on the assumption of steady state are questionable. In contrast, budgets for sediments in the southern California Borderland indicate much higher burial efficiencies, in the range of 50-80%. The Ba:alkalinity (Alk) flux ratio is found to be remarkably constant throughout the environments studied and is indistinguishable from the deep water ratio used for paleoceanographic reconstructions. However, the Ba:organic carbon remobilization ratio is not constant. Combined, these results do not indicate a simple, first-order direct link between Ba and alkalinity remobilization via organic carbon oxidation; however, the similarities in the Ba and alkalinity source functions conspire to maintain the Ba:Alk ratio near the global water column average. This latter observation provides promise for the use of the Ba:Ca ratio in benthic foraminifera as a paleocirculation tracer.

1. Introduction

The marine sediment record contains a potential wealth of information regarding climate change, upper ocean fertility, and ocean circulation through time. Interpreting that record, however, has not proven to be a straightforward task. One of the principal problems with deciphering the geological record is that much of the biogenic material arriving at the seafloor undergoes significant diagenesis, often recycling most of this material back to the overlying water column. To interpret the sedimentary record, it is necessary to identify paleoceanographic tracers that behave in a consistent or predictable fashion during diagenesis. Furthermore, the geochemistry of these tracers and their linkages to other geochemical cycles must be well understood for the modern ocean if we are to interpret tracer patterns for past oceans with confidence.

This paper focuses on the geochemistry of one of the more promising paleoceanographic tools or "proxies": barium. Throughout this paper we will be referring to two different solid phases that contain barium: (1) marine barite ($BaSO_4$) and (2) the barium contained as a trace constituent in benthic foraminifera shells. The primary nondetrital solid phase of barium in the marine environment is barite [e.g., *Dehairs et al.*, 1980; *Bishop*, 1988]. Although the mechanism regulating

barite formation remains enigmatic, generation of microenvironments during the decomposition of biogenic material is the mechanism most frequently advocated [*Dehairs*, 1980; *Bishop*, 1988; *Bernstein et al.*, 1992]. Solid-phase barium formed in the upper ocean sinks to the seafloor where between 0 and >50% of it is preserved, with a mean burial efficiency lying somewhere between 15 and 30% for the world ocean [*Wolgemuth and Broecker*, 1970; *Dymond et al.*, 1992; *McManus et al.*, 1994; *Kumar et al.*, 1996].

Dymond et al. [1992] noted that Ba export from the upper ocean is closely correlated with the export of organic carbon (C_{org}). They further argued that because Ba has a higher burial efficiency than organic carbon, the Ba accumulation rate may be a proxy for paleoproductivity. Sediment records appear to reflect this coupling, as a correlation between the accumulation rate of marine barite and productivity in the equatorial Pacific has been observed [*Goldberg and Arrhenius*, 1958; *Paytan et al.*, 1996]. This correlation indicates a potential for this element to serve as a tool for unraveling the history of upper ocean biological productivity. However this correlation is based on assuming that present-day productivity measurements can be related to accumulation rates averaged through the Holocene. In addition, it should be noted that in using total Ba as a proxy for carbon export, it is assumed that total Ba is a proxy for the biogenic Ba [*Dymond et al.*, 1992] or barite [*Schroeder et al.*, 1997]. It has recently been noted, however, that this assumption may not be valid in the equatorial Pacific region [*Schroeder et al.*, 1997].

A second paleoproxy application is based on measurement of Ba incorporated as a trace constituent in biogenic carbonates. It is assumed that the distribution of deep ocean Ba can be reconstructed for past oceans via measurement of the

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Ba:Ca ratio in benthic foraminifera [e.g., *Lea and Boyle,* 1989, 1990a, 1990b, *Lea,* 1993]. The significance (and appeal) of reconstructing deep-sea Ba records lies in the correlation between Ba and alkalinity (Alk) in modern ocean waters, and the assumption that the foraminiferal Ba:Ca ratio may serve as a tool for reconstructing paleoalkalinity. Reconstructing deep-sea alkalinity has a variety of potential applications for elucidating deep-sea circulation patterns and may reveal information on the paleo-CO_2 system [e.g., *Lea,* 1993]. One assumption inherent in the application of the Ba:Ca ratio as a proxy for paleoalkalinity is that the slope of the present-day relationship remains constant with time. Today, the spatial patterns of Ba and $CaCO_3$ remobilization must be similar (assuming carbonate dissolution is the factor primarily responsible for the global alkalinity distribution) to generate the observed deep water correlation. To keep the relationship unchanged, the spatial patterns of remobilization must remain similar, and the relative quantities of Ba and alkalinity remineralized must not change with time. If these assumptions were true, then perhaps only changes in deep water circulation would influence the Ba-alkalinity relationship and the slope of the present-day Ba-alkalinity relationship would remain constant through time.

This paper will focus on the relationships between Ba remobilization and the recycling of biogenic debris. Previous workers have proposed a number of hypotheses concerning the link between Ba and biogenic debris [*Lea,* 1993; *McManus et al.,* 1994] and this paper presents data that will allow us to test some of the assumptions inherent in using Ba as a paleoproxy. First, we will point out that the equatorial Pacific Ba budget does not balance and that these sediments are currently not accumulating Ba. Second, we will show data demonstrating that Ba preservation is higher in continental margin regions than at sites in the deep ocean. Third, we will show that the Ba:alkalinity benthic flux ratio is relatively constant through a wide range of geochemical conditions. However, we will also demonstrate that the relationship between Ba and C_{org} released during diagenesis is nonlinear, with a decreasing Ba:C_{org} ratio at higher carbon oxidation rates. This latter observation suggests that Ba and alkalinity are not linked via their mutual ties to organic carbon remineralization. Despite the promise of barium as an oceanographic tracer, the factors controlling its preservation and remobilization are still poorly understood. These controls will ultimately influence any interpretation of the paleoceanographic record, whether the paleo-chemical information is present as a trace component in microfossil shells or as a major sedimentary phase.

2. Procedure

2.1. Sample Collection

Elemental fluxes were measured using a free-vehicle benthic lander (Table 1) [*Hammond et al.,* 1996]. The landers used in this study were three-chambered devices [*Berelson and Hammond,* 1986]. Each chamber had a volume of approximately 7 L, covered a surface area of 720 cm², and was stirred with a paddle. Chamber samples were drawn into polyethylene reservoirs at preset times during the experiment.

Once the lander was recovered, trace element samples were filtered (0.45 μm filter) into HCl-leached bottles and subsequently acidified with triple-distilled 6N HCl. Separate splits of this water were also filtered and analyzed for nutrients, pH, alkalinity, ΣCO_2, and Fe (see, *Hammond et al.* [1996], *Berelson et al.* [1996], and *McManus et al.* [1997] for these data sets). Organic carbon oxidation rates were calculated from ΣCO_2, alkalinity, ammonia, and nitrate fluxes [*Berelson et al.,* 1996; *Hammond et al.,* 1996; *McManus et al.,* 1997].

2.2. Sample Analyses

Analyses of dissolved Ba were carried out by isotope dilution-inductively coupled plasma quadrupole mass spectrometry (IDICP-MS) [*Klinkhammer and Chan,* 1990] using a Fisons VG PlasmaQuad Plus at Oregon State University. Analytical precision based on internal monitors was typically better than 2%. Lander measurements have been corrected for dilution (<5%) of chamber water with bottom water during sample withdrawal, and fluxes have been calculated as described by *Hammond et al.* [1996].

2.3. Study Area

This paper presents benthic incubation chamber results from a cruise in the equatorial Pacific region along 140°N (Joint Global Ocean Flux Study (JGOFS) Equatorial Pacific process study) [*Hammond et al.,* 1996]) and from several cruises off the coast of central and southern California (Figure 1). Samples from the central California margin sites were collected along transects through the oxygen minimum zone (~600-1000 m). Bottom water depths for the data discussed here range from 100 to 3700 m, and biogenic remobilization fluxes (e.g., oxygen and silicic acid) vary by nearly an order of magnitude [*Berelson et al.,* 1996; *McManus et al.,* 1997]. The primary goal of our research along the California continental margin was to assess the magnitude of trace element (Mn, Fe, Cu, and Co) and nutrient remobilization fluxes from marine sediments [e.g., *McManus et al.,* 1997].

3. Results

Our study sites include diverse geochemical environments, from the near-shore upwelling regime of the California Current system to the pelagic equatorial upwelling system. These sites encompass ranges in bottom water oxygen concentration, bottom depth, organic carbon respiration, and carbonate dissolution that all vary by more than an order of magnitude (Table 1). Sediments from the California margin have oxygen penetration depths of a few millimeters to tens of millimeters. Equatorial Pacific sediments are oxic to depths of 10 cm or more. Combined, these environments provide a comprehensive geochemical framework from which to address issues related to the sedimentary cycling of Ba.

Although the study sites were diverse, the benthic Ba flux was remarkably constant, with the average (±1 sample standard deviation) from all of our stations equal to 1.12 ± 0.80 μmol m⁻² d⁻¹. Although locations on different cruises varied slightly, several of the stations along the California margin were visited on two occasions. Fluxes measured on

Table 1. Barium Fluxes and Biogenic Debris Decomposition Rates

	Depth	Lat.[a]	Long.[a]	BW O$_2$	Ch.[b]	Ba flux	Ch.[b]	Alk$_c$ flux[c]	C_{ox}	Ba:Alk x 10^3	Ba:C_{ox} x 10^3
Equatorial Pacific (Nov. 1992)[d]											
2S	4475	-1.9	139.7	173	3	0.53 ± 0.09	6	1.13 ± 0.09	0.48 ± 0.11	0.47 ± 0.09	1.10 ± 0.32
Eq	4440	0.1	139.7	172	6	0.80 ± 0.12	9	1.18 ± 0.09	0.47 ± 0.09	0.67 ± 0.11	1.70 ± 0.41
2N	4540	2.1	140.1	171	4	0.85 ± 0.21	8	1.09 ± 0.14	0.59 ± 0.12	0.78 ± 0.22	1.44 ± 0.46
5N	4560	5.1	139.6	175	5	0.43 ± 0.08	9	0.82 ± 0.08	0.13 ± 0.06	0.53 ± 0.11	3.32 ± 2.13
Average (Equatorial Pacific)						0.65 ± 0.10		1.03 ± 0.08	0.42 ± 0.12	0.64 ± 0.11	1.56 ± 0.50
Central California[e]											
CC2-1	97	35.6	121.3	138	1	1.34 ± 0.14	3	1.89 ± 0.59	7.3 ± 1.0	0.71 ± 0.24	0.18 ± 0.03
CC2-2	670	35.2	121.3	18	1	0.63 ± 0.33	3	1.53 ± 0.27	1.1 ± 0.3	0.41 ± 0.23	0.57 ± 0.34
CC3-6	670	35.2	121.3	18	1	0.83 ± 0.25	3	2.06 ± 0.56	2.2 ± 0.8	0.40 ± 0.16	0.4 ± 0.2
CC2-3	1010	35.5	121.6	24	1	0.68 ± 0.11	2	0.85 ± 0.48	0.9 ± 0.8	0.81 ± 0.47	0.76 ± 0.69
CC3-2	1455	36.2	122.4	53	1	1.26 ± 0.35	2	2.71 ± 0.65	2.4 ± 0.9	0.46 ± 0.17	0.5 ± 0.3
CC2-4	2025	36.1	122.4	80	1	0.66 ± 0.22	3	0.95 ± 0.16	1.1 ± 0.3	0.69 ± 0.26	0.60 ± 0.26
CC3-4	2215	36.1	122.5	95	1	0.88 ± 0.26	3	1.70 ± 0.49	1.6 ± 0.7	0.52 ± 0.21	0.6 ± 0.3
CC2-5	3375	36.1	122.6	113	1	0.99 ± 0.63	3	1.00 ± 0.15	0.7 ± 0.3	0.98 ± 0.64	1.41 ± 1.08
CC3-3	3595	36.0	123.0	133	1	0.99 ± 0.18	3	1.32 ± 0.31	0.7 ± 0.4	0.75 ± 0.22	1.4 ± 0.9
Average (Central Margin)						0.92 ± 0.10		1.56 ± 0.20	2.00 ± 0.74	0.59 ± 0.10	0.46 ± 0.18
Southern California (Borderland Basins Region)[f]											
SP	896	33.5	118.4	8	3	1.03 ± 0.15	3	1.62 ± 0.34	1.8 ± 0.4	0.64 ± 0.16	0.6 ± 0.2
SM	905	33.7	118.8	10	1	0.75 ± 0.20	2	1.33 ± 0.36	1.7 ± 0.4	0.56 ± 0.22	0.4 ± 0.2
CC3-8	905	33.7	118.8	9	2	1.26 ± 0.20	2	1.67 ± 0.60	2.0 ± 0.8	0.76 ± 0.29	0.6 ± 0.3
Cat	1300	33.3	118.6	19	2	0.85 ± 0.17	2	0.72 ± 0.46	1.2 ± 0.9	1.19 ± 0.80	0.7 ± 0.6
TB	1514	33.0	119.7	27	1	0.95 ± 0.29	3	1.80 ± 0.43	0.9 ± 0.6	0.53 ± 0.21	1.1 ± 0.8
CC3-12	1515	33.0	119.8	26	2	1.39 ± 0.27	2	1.80 ± 0.52	1.3 ± 0.6	0.77 ± 0.27	1.1 ± 0.5
Cl	2053	32.6	118.1	52	2	2.73 ± 0.70	3	0.61 ± 0.81	1.1 ± 0.3	4.49 ± 6.08	2.5 ± 0.9
CC3-9	2070	32.6	118.1	65	2	4.08 ± 0.45	3	1.17 ± 0.33	0.9 ± 0.4	3.50 ± 1.07	4.5 ± 2.1
PE	3707	32.4	120.6	132	3	0.81 ± 0.11	6	0.50 ± 0.13	0.4 ± 0.1	1.62 ± 0.48	2.0 ± 0.6
CC3-10	3710	32.4	120.6	137	1	0.73 ± 0.11	3	0.70 ± 0.30	0.3 ± 0.4	1.05 ± 0.47	2.4 ± 3.3
Average (Southern Margin)						0.97 ± 0.09		1.27 ± 0.19	1.16 ± 0.20	0.77 ± 0.13	0.84 ± 0.16

Fluxes are in units of mmol m^{-2} d^{-1} except for Ba, which are μmol m^{-2} d^{-1}. Depth is in meters, BW O$_2$ is bottom water oxygen (μM), and Lat. and Long. are latitude and longitude in decimal degrees. Ba:Alk ratios are reported in molar units. Uncertainties are one standard deviation of the mean.

[a]Lat. and Long. are °N and °W, respectively, except where latitudes are negative, indicating °S.

[b]Ch. indicates the number of chambers used in calculating the average value. The first Ch. column is for Ba, and the second is for the biogenic fluxes.

[c]Alk$_c$ is the measured alkalinity flux - ammonia flux.

[d]Bottom water oxygen, alkalinity, and C_{ox} values for the equatorial Pacific sites are from *Hammond et al.* [1996].

[e]Bottom water oxygen, alkalinity, and C_{ox} values for the continental margin sites are from *Berelson et al.* [1996] except for CC3 data; bottom water oxygen and C_{ox} data from CC3 data are taken from *McManus et al.* [1997]. CC2 data were collected in May 1992, Borderland Basin data were collected in March 1994, and CC3 data were collected in November 1995 (exact dates of deployments are given by *Hammond et al.* [1996] and *McManus et al.* [1997]).

[f]Sites from the Borderland Basin region are PE (Patton Escarpment), TB (Tanner Basin), Cat (San Catalina Basin), CI (San Clemente Basin), SP (San Pedro Basin), and SM (Santa Monica Basin). Note that stations CC3-8-12 correspond to the Santa Monica Basin, San Clemente Basin, Patton Escarpment, and Tanner Basin respectively.
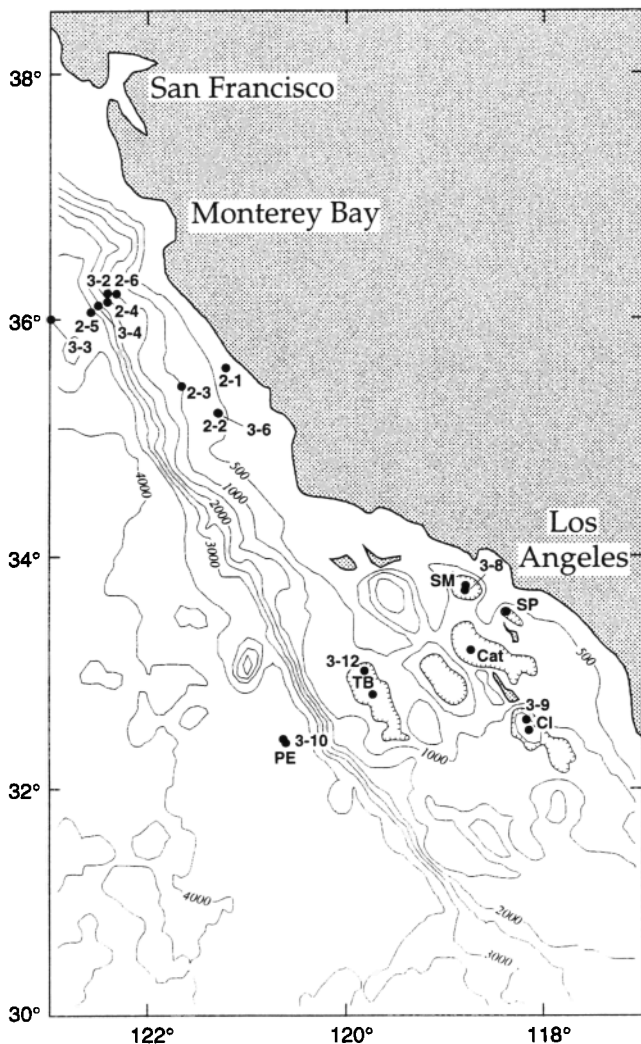
Figure 1. Map of central and southern California study area. Site designations correspond to those in Table 1; the CC designation has been dropped on the map for clarity. See *Hammond et al.* [1996] for map of Joint Global Ocean Flux Study (JGOFS) region.

each visit were within 20% of the mean of both visits, which is within the uncertainty of the measurements (Figure 2). The equatorial Pacific has a slightly lower average benthic Ba flux than the margin sites (Table 1). Only one study site falls outside the sample standard deviation of all study sites: the San Clemente Basin (Stations C1 and T95-9 in Table 1). Although we include the San Clemente data in our discussion, it should be pointed out that these fluxes are about 3 - 4 times greater than the rest of our data set. High fluxes were observed during two consecutive years; thus we have no reason to suspect that these samples were somehow compromised. The cause of the high fluxes is enigmatic.

4. Discussion

4.1. Ba Cycling in the Equatorial Pacific

This study presents the first in situ measurements of the benthic Ba flux from sediments underlying the high-

productivity region of the equatorial Pacific. The pattern of the Ba flux across the equatorial Pacific (Figure 3) is similar to that of the biogenic components [*Hammond et al.*, 1996], with the highest flux centered near the equator and lower fluxes at the higher latitudes. This pattern is not surprising given that the transport of solid-phase Ba to the sediments from the upper water column is at least semiquantitatively related to carbon export [e.g., *Dymond and Collier*, 1996].

A comparison of the rain, accumulation, and regeneration rates of Ba in this region demonstrates that the barium budget is not currently balanced as the sum of regeneration plus accumulation is about twice the rain rate (Figure 3). Note that we used the barite accumulation rate, rather than the total Ba accumulation rate, because barite is the dominant sedimentary solid phase and should approach the total Ba accumulation rate for this region. However, the barite accumulation rate is a minimum estimate for the Ba accumulation rate [*Schroeder et al.*, 1997], thus making the observed budgetary imbalance even more disparate.

The different data sets cover radically different timescales. Benthic flux measurements were made over a few days in late 1992, although they should characterize a much longer period that is defined by the (currently unknown) length of time required for dissolution of the reactive barium phases in sediments. Sediment trap data in Figure 3 is the average of a 1 year deployment during 1992; earlier measurements made during 1982-1985 indicated comparable fluxes of 0.6-0.9 μmol m^{-2} d^{-1} at 1°N and 0.4 μmol m^{-2} d^{-1} at 11°N. *Berelson et al.* [1997] have used sea surface temperature (SST) as a normalization tool and suggested that the 1992 JGOFS traps were deployed during a period when biogenic fluxes were only 75-85% of the mean for the past 50 years. An adjustment of this amount to convert Ba rain rates in Figure 3 to a 50 year average would still leave a substantial imbalance. Over long timescales the barium budget must balance, but the contrast between average Holocene accumulation and present (rain - remineralization) demonstrates that little or no barium is currently accumulating and the contemporary barium cycle in equatorial Pacific sediments is not at steady state. The observation of an unbalanced Ba budget is consistent with similar observations for calcium carbonate in these sediments. In the case of carbonate, several lines of evidence suggest that there is net chemical erosion of carbonate in this region
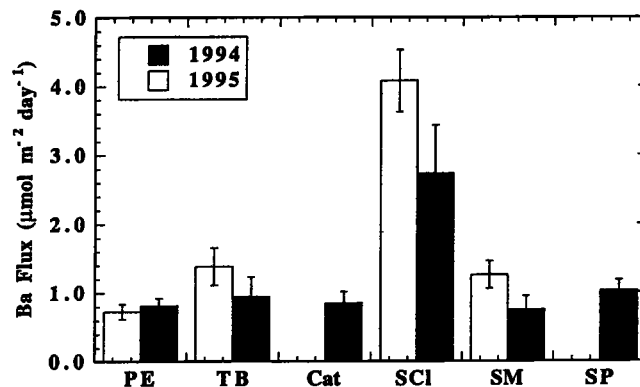

Figure 2. Ba flux at southern California margin sites for 1994 and 1995. Locations are given in Table 1.
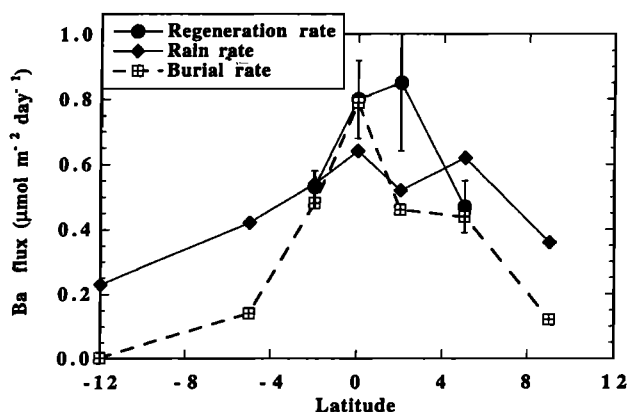
Figure 3. Ba regeneration, rain, and accumulation rates as a function of latitude from the JGOFS study region. Note the imbalance in the Ba budget. Rain rate data are from *Dymond and Collier* [1996] and accumulation rate data are from *Paytan* [1995].

[*Berelson et al.*, 1997]. On the basis of models for ^{230}Th behavior, the onset of carbonate erosion in the equatorial Pacific was ~3000 years ago [*Berelson et al.*, 1997]. While we recognize carbonate erosion in this region does not necessarily imply that all budgets are out of balance (note that both the opal and organic carbon budgets are balanced within the limits of the data [*Berelson et al.*, 1997]), it is clear from the combined sediment trap, lander, and barite accumulation data sets that the Ba budget is not currently in balance.

One implication of these findings is that paleoproductivity models calibrated with steady state sediment accumulation rates for the late Holocene and contemporary rates of surface water processes in this region must be considered suspect. In addition, although the Ba budget must achieve a balance in the long term, if the efficiency of burial is a function of the accumulation rate as suggested by *Dymond et al.* [1992] and the accumulation rate varies through time, the relation between Ba accumulation and rain rate will probably not be monotonic. This additional caveat would also make it difficult to extract paleocarbon export information from barium accumulation rates alone.

4.2. Ba Cycling Along the Southern California Margin

The benthic flux of barium within the southern California region is relatively constant (~1 μmol m^{-2} d^{-1}; Figure 2). The one exception to this general trend is in San Clemente Basin, where the Ba flux is as much as a factor of 4 times the typical

rate for this region. By using the benthic flux data and the sedimentary Ba and Al concentrations with published sediment accumulation rates we can construct budgets for each of the regions where we have complete data sets (Table 2). This approach assumes that over the time scales of sediment accumulation at these sites, the Ba budget is at steady state. Also, we have assumed that the Ba associated with detrital material can be estimated by assuming that the Ba:Al ratio is 0.0075 [*Dymond et al.*, 1992; *Thunell et al.*, 1994] and that the difference between this "detrital" component and the total Ba is derived from upper ocean biological processes (Ba-bio). From a paleoproductivity point of view it is the cycling of this Ba-bio component that is of interest. The assumed Ba:Al ratio will impart a significant uncertainity in the Ba budgets for San Pedro and Santa Monica Basins because for these near-shore basins there is a substantial correction for the detrital fraction (>50%). While the assumed Ba:Al ratio is consistent with that assumed by others [e.g., *Dymond et al.*, 1992; *Thunnel et al.*, 1994], we should point out that the average Ba:Al ratio for northern California rivers is 0.0092 [*Dean et al.*, 1997]. With this information in mind, the preservation of Ba-bio considered here is likely to represent an upper limit, and for the near shore basins in particular, preservation could be much lower than those values presented in Table 2.

For San Pedro Basin, *Thunnel et al.* [1994] present sediment trap Ba data for the period between January and July 1988. Their trap results provide an additional budgetary constraint for this basin and indicate a Ba-bio rain rate of ~2 μmol m^{-2} d^{-1}, which when coupled with either the benthic flux or the sediment accumulation rate data yields a burial efficiency of ~50% (this comparsion also assumes a Ba:Al detrital ratio of 0.0075 for both the sediment trap and sediment data). Thus, within the constraints of the data (and unlike the Equatorial Pacific data) the San Pedro system demonstrates an excellent budgetary balance.

Our interest in establishing the Ba budget is partly motivated by the hypothesis that Ba preservation is a function of the sediment mass accumulation rate [*Dymond et al.*, 1992]. At low mass accumulation rates (MAR) (in μg cm^{-2} y^{-1}) the fraction of Ba preserved in the sediments is predicted to be low (<10%), increasing with MAR:

$$\%Ba\ preserved = 20.9log(MAR) - 21.3 \qquad (1)$$

If this algorithm accurately predicts preservation, then we would expect there to be greater preservation in the near-shore sites of the southern California Borderlands region as compared to those sites further offshore where mass

Table 2. Sediment Characteristics and Composition for the Southern California Margin

Station[a]	Sed. Acc. Rate,[b] mg cm^{-2} yr^{-1}	Ba, ppm	Al, %	Mn, ppm	Ba:Al	Ba-bio,[c] ppm	Ba acc. Rate, μmol m^{-2} d^{-1}	Benthic Flux μmol m^{-2} d^{-1}	% preserved
SP	13	966	7.46	423	0.013	407	1.1	1.0	51
SM	16	862	6.60	372	0.013	367	1.2	0.8 - 1.3	47 - 59
SCl	15	2678	6.42	2423	0.042	2197	6.4	2.7 - 4.1	62 - 71
Cat	14	1503	6.47	407	0.023	1018	2.8	0.9	76
TB	12	1781	3.33	151	0.053	1531	3.7	0.9 - 1.4	72 - 80
PE	3	4988	7.03	2886	0.071	4222	2.7	0.8	77

[a] Sediment depths for samples are 5.5 cm for SM, SCl, TB, and PE and are 6 and 8 cm for SP and Cat.
[b] Sediment accumulation rates are taken from Berelson et al. (1996).
[c] For calculation of Ba from upper ocean biological processes (Ba-bio) we have assumed a Ba:Al ratio in detrital material of 0.0075.

accumulation rates are lower. Although considerable uncertainty is present in the burial term, this hypothesis is contrary to the trend in Table 2.

The salient feature of the preservation data for both the southern California margin and the equatorial Pacific is that mass accumulation rate is not acting as a master variable for Ba preservation in these environments. In the case of the equatorial Pacific, if the sediment trap data and lander data are correct, contemporary preservation is essentially zero. For the southern California margin, essentially only the Patton Escarpment site has a sediment accumulation rate that is significantly different from the other locations, yet both Santa Monica and San Pedro Basins have lower Ba preservation efficiencies than the other basins in this region. We suggest that the lower preservation efficiencies along the margin could be related to a diagenetic remobilization of Ba [McManus et al., 1998].

We must also recognize that there are a number of factors that could cause artificially high Ba burial efficiencies in this region. Because Ba may be associated with manganese oxides, sedimentary Ba concentrations could be influenced by a diagenetic sequestering of Ba with this phase [e.g., Schroeder et al., 1997]. In this case, remobilized Ba could be "trapped" on near-surface oxides, thus increasing the apparent Ba burial efficiency. However, there is no clear correlation between sediment Mn and the fraction of Ba preserved (Table 2). For example, both Tanner Basin and Patton Escarpment have comparable burial efficiencies, yet their sediment Mn concentrations differ by more than an order of magnitude. Certainly, an association with Mn oxides is possible, but it is clear that such an association cannot be the sole influence on Ba burial in this region. Another possible source of Ba to the sediments in the southern California region could be from fluid expulsion associated with cold seeps or from deeper remobilization of barium in the zone of sulfate depletion followed by authigenic precipitation of barite in the near-surface sediments [e.g., Torres et al., 1996a, b]. For example, in San Clemente Basin some process other than simple rain from the surface ocean must be contributing to the total Ba budget. We make this argument because the remobilization plus burial term for this basin is ~10 μmol m^{-2} d^{-1}, a number which is much larger than any other measured in the North Pacific [e.g., Dymond et al., 1992; Thunnel et al., 1994; Dymond and Collier, 1996]. In addition, barite "concretions" [Revelle and Emery, 1961] and "tall piles" of surface sediment barites [Lonsdale, 1979] have been reported as occurring within this basin. Such observations are consistent with a model of authigenic barite formation in continental margin regimes due to deep dissolution of barite in the sulfate reduction zone followed by either diffusive or advective transport to the upper sediment column [Torres et al., 1996a, b]. We present this discussion as a caveat to interpreting any Ba burial data in continental margins, in particular active margins; that being said, the budgetary importance of any authigenic redistribution process at our study sites remains unknown.

From a paleoceanographic perspective, reconstructing and interpreting Ba records in continental margin environments is laden with potential difficulties. Although some data presented here and elsewhere suggest that mass accumulation rate may play a role in Ba preservation, its relative importance

remains uncertain, and it is clearly suspect as a "master" variable. For example, the margin regions exhibit higher preservation than the equatorial Pacific, yet, along the margin, the preservation of Ba is high at the site with the lowest sediment accumulation rate (Patton Escarpment). In addition, it has also been suggested that as sulfate reduction becomes an increasingly important process for the oxidation of organic material, the burial efficiency of Ba will decrease [McManus et al., 1998]. Given these difficulties and the apparent budgetary problems with Ba in the equatorial Pacific, we must conclude that Ba (and possibly barite) is unreliable as the sole tool for reconstructing paleoproductivity; however, in concert with other tracers it may yet prove to be useful in certain environments.

4.3. Ba:Alk Remineralization Ratio

Lea and Boyle [1989] have proposed that the Ba:Ca ratio in benthic foraminifera may be a suitable tracer for paleoalkalinity distributions. This proposal is based on an observed correlation between Ba and alkalinity throughout the modern world ocean and a correlation between the Ba:Ca ratio in benthic foraminifera and bottom water Ba concentrations. Despite the relatively consistent nature of the Ba:Alk ratio [Lea, 1993], a mechanism explaining the covariation between these two constituents has remained elusive. Some insight may be gained by considering a two-box ocean model. The steady state balance for any parameter shows that the concentration contrast between surface and deep waters is

$$C_{deep} - C_{surf} = \frac{Jp - B/A}{w} \qquad (2)$$

where C is dissolved concentration, Jp is the particulate rain per unit area (mol m^{-2} y^{-1}), A is ocean area (m^2), B is the burial rate (equal to river input, mol y^{-1}), and w is the vertical mixing rate of water (m y^{-1}). Defining burial efficiency as

$$E = B/J_p A \qquad (3)$$

indicates that

$$\frac{(Ba_{deep} - Ba_{surf})}{(Alk_{deep} - Alk_{surf})} = \{\frac{J_{PBa}}{J_{PAlk}}\} \{\frac{1 - E_{Ba}}{1 - E_{Alk}}\} \qquad (4)$$

This simple analysis indicates that the average increase in deep waters depends on the rain ratios of Ba and CaCO$_3$ (its dissolution is the primary source of alkalinity in the deep sea [Horibe et al., 1974]) and the efficiencies of regeneration of each constituent in the deep sea. Furthermore, as pointed out by Lea and Boyle [1990a], the close correlation between Ba and alkalinity in deep waters indicates that the spatial variations of their rain ratios and regeneration efficiencies must be similar.

The covariations in rain rates observed in equatorial Pacific sediment traps are plotted in Figure 4a. Means for these stations differ only slightly from the increase observed in deep waters. Consequently, as shown by equation (4), the similarity of the relationships for raining particles and deep waters (Figure 4a) indicates that quite similar fractions of each must be regenerated. This point can also be demonstrated from
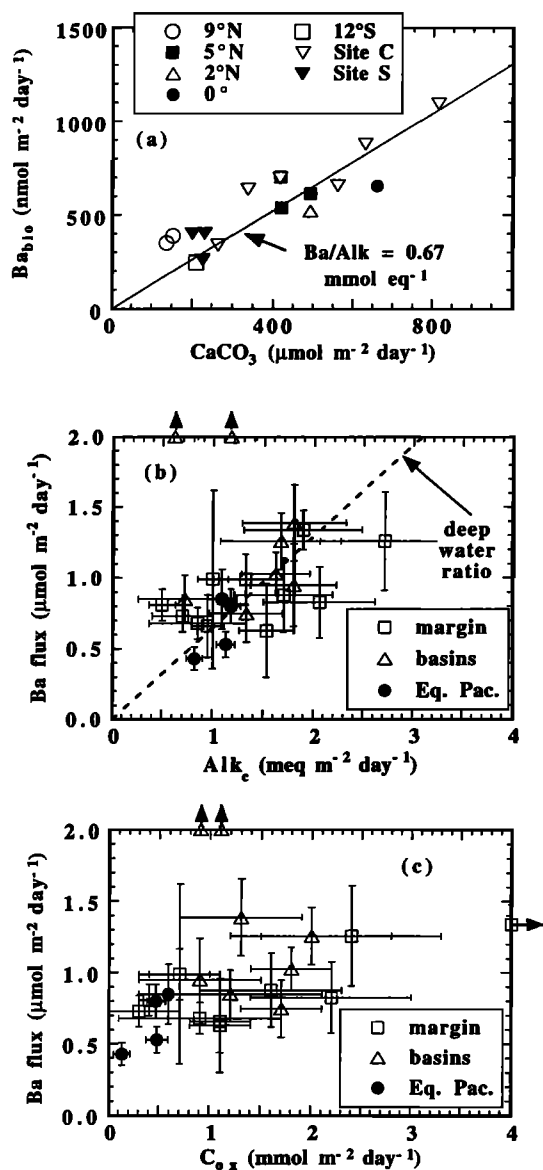
Figure 4. (a) Barium and $CaCO_3$ covariance in sediment traps from the equatorial Pacific. Data represent averages of Ba-bio versus averages of $CaCO_3$ in traps deployed between 1 and 3 km depth for periods of ~1 year. JGOFS data (stations indicated by degrees latitude) represent an annual average from February 1992 to January 1993 at one to three depths from 1200 to 3800 m. The site C data (1°N and 139°W) represent two periods of deployments (December 1982 to February 1984, February 1984 to May 1985) at three depths from 1100 to 3500 m. The Ba fluxes from the first period averaged ~65% of the second period. The site S data (at 11°N and 140°W) are about 1 year (December 1982 to February 1984) at three depths from 700 to 3400 m. Data sources are JGOFS [*Dymond and Collier*, 1996; *Honjo et al.*, 1995] and for Sites C and S, *Dymond and Collier* [1988] and *Dymond et al.* [1992]. The line is the slope of the regression given by *Lea* [1993] describing the average slope of the Ba versus alkalinity relation for ocean waters. (b) Ba:Alk ratio for all study sites. The line represents the ratio used for paleoalkalinity reconstructions. (c) Ba as a function of the organic carbon oxidation rate.

a slightly different approach. Most of the alkalinity input to deep waters comes from carbonate dissolution [*Horibe et al.*, 1974], and most of this dissolution occurs in sediments [*Berelson et al.*, 1994]. The fraction of the carbonate rain into

waters deeper than 200 m that is buried is depth-dependent but has been estimated by *Broecker and Peng* [1982] to be about 20% and by *Milliman* [1993] to average about 46%. Thus 54-80% of the carbonate rain is regenerated. The Ba budget of *Paytan and Kastner* [1996] suggests that its burial efficiency should be approximately 33%, and most regeneration must come from the seafloor, as shown by *McManus et al.* [1994] and in this paper. Consequently, about 67% of the Ba rain is remineralized, and the ratio of the regeneration efficiencies in equation (4) is about 1.0 with an uncertainty of about 25%.

The spatial coherence between barium and alkalinity regeneration can be roughly evaluated. To a first approximation, Ba fluxes in the margins and the open ocean are similar (Table 1). Similarly, *Berelson et al.* [1994] noted that carbonate dissolution per unit area is relatively constant; these findings are consistent with the close correlation between Ba and alkalinity in bottom waters [*Lea*, 1993]. Like carbonate, Ba burial efficiency seems to be depth-related. A simple budget for Ba burial (Table 3) can be created by dividing the ocean below 200 m into three categories: open ocean areas (>4 km depth) with low sediment accumulation rates where nearly all of the carbonate and Ba rain dissolves, intermediate areas (3 - 4 km depth) with oxic respiration where a portion of the carbonate and Ba rain dissolves, and margin areas (0.2-3 km depth) where 50-80% of the Ba rain is preserved. JGOFS stations characterize the first group and provide Ba:Alk data consistent with trap measurements. We have not obtained data from the second group, but if we assume that as the fraction of carbonate rain that is buried increases, causing higher sediment accumulation rates, the Ba burial fraction might exhibit a similar increase. As noted earlier, sediment accumulation rate is probably not the dominant variable determining the Ba burial fraction, but it is likely that it plays an important role in limiting the time in which barite can easily communicate with bottom waters that contain lower Ba concentrations than pore waters. In the third group the relationship between Ba and alkalinity regeneration is similar to deep water relations (Figure 4b), although the mechanism causing this similarity is unknown because much of the alkalinity flux from these anoxic sediments does not come from carbonate dissolution. This budget for Ba burial (Table 3) is consistent with the whole ocean estimate of E_{Ba} = 33% noted above, and indicates that most Ba burial must be in margin sediments. Given the relative paucity of data, this budget must be considered a starting point for future discussion and work.

An evaluation of correlations between Ba benthic fluxes and other parameters may help to determine if a mechanism exists to fix the Ba-alkalinity relationship. Evaluating the relationship between Ba and alkalinity benthic fluxes requires some adjustments. At some of our sites a portion of the alkalinity flux is attributable to ammonia. Any ammonia released from the seafloor will be quickly oxidized into nitric acid in the lower water column, neutralizing some of the alkalinity. Consequently, we have plotted Ba fluxes versus alkalinity corrected for ammonia (Figure 4b). Station averages, based on 1-9 chambers at each site, have been used. The results in Figure 4b illustrate consistency with the relationship observed in bottom waters. It is not surprising

Table 3. Estimates of the Pacific Ocean Ba Budget

Depth Zone	Area,[a] 10^6 km^2	% Area	% Ba Rain[b]	% Ba Buried[c]	E_{Ba}[d]
0.2 - 3 km	16.7	13	31	65	20
3 - 4 km	36.2	23	18	33	6
> 4 km	102.1	64	51	0	0
Total	155.0	100	100		26

[a] *Menard and Smith* [1966].

[b] The 0.2-3 km depth zone is assumed to be margin area, and Ba rain in this zone is assumed to be 3 times higher than in the rest of the ocean, on the basis of an average burial efficiency of 65% and a benthic flux that is similar to the open ocean.

[c] The Borderland data is chosen to represent the 0.2-3 km depth zone, the equatorial Pacific is assumed to represent the >4 km zone, and the 3-4 km zone is assumed to have a burial efficiency between the other two.

[d] Contribution of each zone to the burial of Ba in the Pacific. This is calculated as the product of the two preceding columns.

that the JGOFS equatorial Pacific flux data are consistent with bottom water relationships, given that the Ba:CaCO$_3$ rain ratio is also consistent with this value and most (if not all) of the Ba and carbonate rain dissolves in these sediments. The mean of this group (Table 1) of 0.64 ± 0.11 mmol eq^{-1} is indistinguishable from the mean bottom water ratio of 0.67 mmol eq^{-1} [e.g., *Lea*, 1993].

While we have noted that the Ba flux is relatively constant through a wide range of environments, the alkalinity flux is also relatively constant. However, the significant point with respect to this paper is that the contributions to the alkalinity budget change significantly through these different regions. In the equatorial Pacific, nearly all of the alkalinity is supplied via carbonate dissolution. In reducing sediments, 30-80% of the alkalinity flux is supplied by net nitrate or net sulfate reduction, rather than carbonate dissolution [*Berelson et al.*, 1996]. Given this fact, it is surprising that data from the central and southern California margins are similar to the bottom water ratio, as they have means of 0.59 ± 0.10 and 0.77 ± 0.13 mmol eq^{-1} respectively. The similarity between the Ba:Alk flux ratio and the deep water ratio was noted by *McManus et al.* [1994] and attributed to a possible linkage between Ba and C$_{org}$ [*Lea*, 1993]. With more data now available (Figure 4c; Table 1), there does not appear to be a clearly defined linearity between Ba and C$_{org}$ remineralization in sediments, reflecting the nonlinearity in the rain ratios as noted by *Dymond and Collier*. [1996]. Note that while the data in Figure 4c may appear linear, this relationship should pass through the origin, thus requiring nonlinearity in the relationship; furthermore, note in Table 1 the nearly factor of 10 variability in that ratio, and, in particular, note the lower Ba:C$_{ox}$ ratios at higher C$_{ox}$ values.

In summary, it seems likely that the rain of Ba is largely defined by upper ocean processes. In the Pacific most of the Ba

rain appears to be remobilized. Similarly, most of the carbonate raining to the seafloor is dissolved. This similarity in regeneration patterns thus leads to the covariation between deep water Ba and alkalinity. Their remineralization ratio may be fixed in some (ill-defined) way by the ratio of barite export to carbon export. Ultimately, it is the latter that determines the benthic alkalinty flux. The deep water Ba:Alk ratio could change if the Ba:carbonate rain ratio changes, or if the burial efficiencies of either constituent changes substantially. However, the burial efficiencies may be less sensitive to change if the accumulation rate of carbonate in open ocean sediments is a major factor in regulating the burial efficiency of barium, a hypothesis which remains to be confirmed. A change in burial efficiency might also be required if the riverine input of Ba was altered. Given the short residence time of barium (10^4 years), if Ba input changed and there was no change in factors governing the Ba rain, the burial efficiency would rapidly change. Despite the difficulties in elucidating a mechanism linking Ba and alkalinity regeneration, if the Ba:Alk ratio is somehow tied to the relative burial efficiencies of these components, then only large changes in the Ba or alkalinity burial terms will force a global-scale change in this ratio. More sophisticated modeling of the Ba-alkalinity system will be required to understand the sensitivity of the Ba:Alk ratio to changing environmental conditions. Such a modeling effort is beyond our current understanding of Ba geochemistry.

5. Conclusions

The application of any paleoproxy necessitates an understanding of the fundamental geochemistry of that proxy. This paper has focused on three fundamental assumptions regarding the use of barium as a paleoproxy: (1) the rain, regeneration, and accumulation rates are balanced, i.e., are at steady state, (2) Ba burial efficiency is uniquely related to sediment accumulation rate, and (3) the Ba to alkalinity remineralization flux ratio is constant. Our data indicate that the first two assumptions are not valid. Clearly, the equatorial Pacific sediments are not at steady state, and a site in San Clemente Basin does not appear to be in steady state. While it is propitious that the Ba:Alk regeneration ratio remains fairly constant through a variety of geochemical conditions, the apparent lack of a functional (linear) relationship between Ba and organic carbon implies that the Ba:alkalinity relationship is not tied in a simple fashion to their mutual coupling with C$_{org}$. Ultimately, any whole-ocean chemical change that alters the burial efficiency of either Ba or alkalinity could also result in a change in the Ba:Alk slope.

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